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Title: Reaction between Criegee intermediates and hydroxyacetonitrile: Reaction mechanisms, kinetics, and atmospheric implications
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Responses in blue.

CC: 2

This manuscript describes new quantum chemical and computational kinetics calculations that show that reactions of carbonyl oxides are likely to play a significant role in the atmospheric transformations of hydroxyacetonitrile. The calculations are of high reliability and the conclusions are of substantial interest for understanding atmospheric reactions of wildfire products. I recommend publication of the manuscript and have some suggestions for clarification.

1.First, the basis for assessing that hydroxyacetonitrile is in fact a significant atmospheric product in wildfire burning is half described — either the authors should simply refer to the publications that treat the analytical chemistry behind the assignment and its revision (which are lucidly described in the referenced reports) or they should go into more detail here. I would lean towards the first option, but as it is in the current manuscript the story is very confusing.

Author response: Thanks for your comments. What we mean here is that the CH_3NCO detected previously is actually $HOCH_2CN$ in the atmosphere by the work of Finewax et al, so the source of CH_3NCO emissions in the atmosphere is actually the source of $HOCH_2CN$. We have modified the sentence to "Hydroxyacetonitrile ($HOCH_2CN$), a reactive nitrogen-containing compound, has recently been identified as a C_2H_3NO isomer. Earlier field measurements had attributed the C_2H_3NO signal to methyl isocyanate (CH_3NCO) when using chemical ionization mass spectrometry (CIMS) (Priestley et al., 2018; Mattila et al., 2020; Wang et al., 2022) , as CIMS is insensitive to the detection of isomers, and thus cannot differentiate between the isomers of CH_3NCO and HOCH2CN. However, very recent detection with I^- chemical ionization mass spectrometry (I-CIMS) identified the C_2H_3NO signal as $HOCH_2CN$ (Finewax et al., 2024)." and "In other words, the CH_3NCO detected in the atmosphere is essentially $HOCH_2CN$. Therefore, the atmospheric sources of CH_3NCO from previous investigations are actually the sources of $HOCH_2CN$. Consequently, $HOCH_2CN$ is emitted in chemicals released from biomass burning, such as wildfires and agricultural fires, as well as in bleach cleaning environments (Mattila et al., 2020; Priestley et al., 2018; Wang et al., 2022a; Koss et al., 2018; Papanastasiou et al., 2020)." in line 27-30 on page 2.

2.Second, the manuscript treats simply the control of atmospheric removal of hydroxyacetonitrile, but the implications of this reaction for atmospheric chemistry depend also on the fate of the products and on the (still highly uncertain) tropospheric concentration of carbonyl oxides. The present calculations show a sequence of energetically accessible unimolecular transformations (not really "decomposition") of the initial product. I am wondering if the authors could describe for completeness the lowest bimolecular channels of the reaction, and whether the fate of any of the proposed isomeric products would be expected to have different consequences for the atmosphere or environment than the others.

Author response: Thanks for your comments. The large exothermic, unimolecular conversion of the intermediate M1 formed from CH_2OO + $HOCH_2CN$ is dominant for the formation of the final product, where the rate-determining step is TS1, which similar to the alkene-ozone reaction (Nguyen et al., 2015). We have added the comment in the revised version "Furthermore, the rate-determining step for the formation of the final product from the CH_2OO + $HOCH_2CN$ reaction has been identified as the initial step, which is similar to the reaction of alkenes with ozone(Nguyen et al., 2015)." In line 226-227 on page 10.

3. Also, given that the reaction with OH would be competitive in many environments, would the products of that reaction have different implications than the products of this reaction? I understand that this stretches the boundaries of the work, and perhaps the authors will consider it out of scope, but in an atmospheric chemistry journal I think a bit of additional context in the conclusion section would be fitting.

Author response: Thanks for your comments. We have done some additional calculations. As a result, the final products of the reaction between $HOCH_2CN$ and CH_2OO differ from those of the reaction with OH. The dominant products of the reaction between $HOCH_2CN$ and OH are H_2O and HOC(H)CN, which further reacts with O_2 to ultimately yield hydroperoxyl radical (HO_2) and formyl cyanide (HC(O)CN). However, the reaction of $HOCH_2CN$ with CH_2OH undergoes multiple chemical processes to form $HC(O)NHC(O)CH_2OH$, which finally leads to formation of carbon monoxide and glycolamide. These products are potential toxic air pollutants and significant contributors to atmospheric organic aerosols. We have added some comments in the revised version. "Then, the three-member ring intermediate M3 then undergoes two different reaction routes. One is open-ring coupled hydrogen shift to form M4 via the transition state M3-TSc. The other is analogous to that proposed by Franzon et al. (Franzon et al., 2023), which is an open-ring coupled bond breaking to form HCHO and $HOCH_2NCO$ via the transition state M3-TSc1. However, $\Delta H_0^{\ddagger}$ for M3-TS3c is 11.97 kcal/mol lower than that of M3-TSc1. Therefore, M3-TSc is the dominant reaction pathway for the unimolecular reaction of M3. Moreover, IRC calculations also show that M3-TSc connects well with M3 as described in Figure S3. Subsequently, the H atom of the intermediate OH on intermediate M4 is transferred to the N atom to yield the intermediate species M5. Then, the process was depicted in Fig. 3. The calculated enthalpy of reaction at 0 K of M5 is –86.55 kcal/mol, indicating the unimolecular isomerization is thermodynamically driven. Intermediate M5 undergoes unimolecular isomerization via two different pathways. In the first pathway, an intramolecular hydrogen transfer from the aldehyde group to the central carbonyl oxygen is followed by C–N bond cleavage, yielding CO and intermediate M6. Then, hydrogen shift of OH in M6 to NH group leads to the formation of glycolamide. Alternatively, a second pathway involves hydrogen migration from the aldehyde group to the central carbon atom, accompanied by C–N bond rupture, producing HNCO and glycolaldehyde. The formation of carbon monoxide proceeds with a significantly lower activation enthalpy (−54.19 kcal/mol) compared to that for glycolaldehyde (−32.32 kcal/mol), indicating that the CO-forming channel is kinetically favored." in line 212-226 on page 10. "The reaction products of $HOCH_2CN$ with OH radicals exhibit significant differences from those formed by the reaction of CH_2OO with $HOCH_2CN$. The main products of the $HOCH_2CN$ + OH reaction are H_2O and the HOC(H)CN radical, which subsequently reacts with O_2 to yield HO_2 and formyl cyanide (HC(O)CN) (Marshall and Burkholder, 2024). In contrast, the reaction of $HOCH_2CN$ with CH_2OO proceeds through chemical transformation processes, ultimately forming CO and glycolamide. Glycolamide is an amide, which can contribute to the formation of secondary organic aerosols and an important interstellar molecule (Joshi and Lee, 2025; Sanz-Novo et al., 2020; Yao et al., 2016)." in line 299-304 on page 14. "Simultaneously, we show that the final product in the CH_2OO + $HOCH_2CN$ reaction is glycolamide and CO, where glycolamide could contribution to the formation of secondary organic aerosols." in line 323-324 on page 15.

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